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論文特集「高機能両親媒性化合物の合成とその高次構造」

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疎水性炭化水素鎖を含むシリカゲルの合成とその構造

(1990年5月8日受理)

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ゾル-ゲル法により、テトラメトキシシランとオクチルトリエトキシシランから疎水性炭化水素鎖を含むシリカゲルを合成した。界面活性剤水溶液と同様、このようなシリカゲル中では疎水性炭化水素鎖が集合体を形成すると考えられる。そこでゲル中に色素(4-ヒドロキシアゾベンゼン)を溶かし込み、そのスペクトル測定を行うことにより、ミセル状集合体の形成を検討した。さらに新規無機-有機複合材を作製する目的で、高沸点の液晶物質を溶かし込み、その熱的性質を調べた。

1 緒言

近年、ゾル-ゲル法を用いた無機材料の合成について多くの研究報告がだされてきた¹⁾。これらの多くはゾル-ゲル法により望みの組成のゲルを作製し、その後ゲルを高温熱処理することにより希望の組成をもつ無機材料を合成するものである。ゾル-ゲル法で作製されたゲルは多孔性であり、このままでは機械的強度が低く、またゲル中の溶媒の蒸発にともない体積が収縮するが、高温熱処理することにより、緻密で堅ろうな材料が得られる。

ゾル-ゲル法は室温程度の比較的低い温度で、無機材料を合成できることが大きな特徴であり、この特徴を生かす一つの方向として有機-無機複合材料の合成が考えられる^{2,3)}。高温熱処理操作を施さなければ、無機材料中に有機化合物を含む新しい複合材料の合成が可能である。そこで本研究では、長鎖の炭化水素鎖として炭素数8のオクチル基を含むシリカゲルの合成を行い、シリカゲル中で炭化水素鎖が形成する集合状態について検討した。さらに、合成したシリカゲル中に液晶を溶かし込むことにより、温度応答性をもつ材料の作製、並びにゲルの収縮抑制を検討した。

2 実験

2.1 オクチル基を含むシリカゲルの合成とその構造解析

テトラメトキシシラン (TMOS: Petrarch Systems), オクチルトリエトキシシラン (C8: Petrarch Systems), 4-ヒドロキシアゾベンゼン (HAB: 東京化成, 特級) を購入し、そのまま使用した。HAB を乾燥エタノールに溶解し、0.05 mmol/dm³ の溶液 A とした。TMOS 2.44~2.60 g, C8 0~0.4 g をそれぞれ正確に秤量し、10 ml の試料瓶中でよく混合した。TMOS と C8 の割合を表1に示す。さらに溶液 A 1.6 ml と 13 wt% の塩酸 1.43 ml を

加え、振とう器を使ってかきまぜた。このとき発熱するが、これを数分間放置して、温度が室温程度に下がってから、10 mm×10 mm 角ポリメタクリレート製 UV セル (Hellma) に入れてテフロンシールテープ (ニチアス, 厚さ 0.1 mm) で封じた。参照側を純水とし、日立 340 紫外可視分光光度計で 300~600 nm におけるスペクトルを測定した。

2.2 液晶を含むシリカゲルの作製

10 ml 試料瓶中で TMOS 2.44~2.60 g, C8 0~0.4 g, エタノール 1.6 ml, 純水 1.2 ml を混合し、密封して室温で放置した。なお、触媒 (塩酸) を加えなかったため、ゲル化するのに2~3日を要した。ゲルの上方から無水のエタノールを適量滴下し、翌日そのエタノールを捨てて新しいエタノールと交換した。この操作を5回以上くり返し、ゲル中の溶媒をエタノールと置換した。なお、この過程においてゲルの体積変化は認められなかった。

次に、上記のゲル中のエタノールを液晶で置換した。なお、置換に要する液晶の量はあらかじめ反応溶液調製時の TMOS から生成する SiO₂ (比重 2.20) の体積を計算しておき、ゲル全体の体積からこの体積を引いて空隙率を求めて決定した。液晶は *N*-(4-Methoxybenzylidene)-4-butylaniline (MBBA; Aldrich Chem., 比重 1.027) を用いた。栓をゆるめた状態にしておくと、エタノールの蒸発にともない MBBA がゲル中に浸透し、2~3日経過すると淡黄色の固体が得られた。DSC 測定には Perkin Elmer DSC-II を用い、窒素雰囲気下、昇温速度 5°C/min で測定した。

Table 1 Preparation conditions of samples

Amount of C8 (mol%)	TMOS (g)	C8 (g)	Ethanol (ml)	HCl ^{a)} (ml)
0	2.60	0	1.6	1.4
1	2.57	0.042	1.6	1.4
2	2.55	0.094	1.6	1.4
3	2.52	0.141	1.6	1.4
4	2.50	0.188	1.6	1.4
5	2.47	0.235	1.6	1.4
6	2.44	0.282	1.6	1.4
7	2.42	0.329	1.6	1.4

a) 13.2 wt% HCl solution.

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- 1) 作花 清夫, "ゾル-ゲル法の科学", アグネ承風社(1988).
- 2) G. Philipp, H. Schmidt, *J. Non-Crystal. Solids*, **63**, 283(1984).
- 3) D. Avnir, D. Levy, R. Reisfeld, *J. Phys. Chem.*, **88**, 5956(1984).
- 4) 谷 俊朗, セラミックス, **21**, 111(1989).

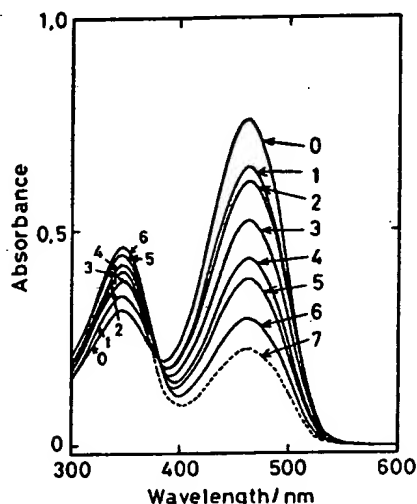


Fig. 1 Absorption spectra of HAB solubilized in C8-containing silica gels

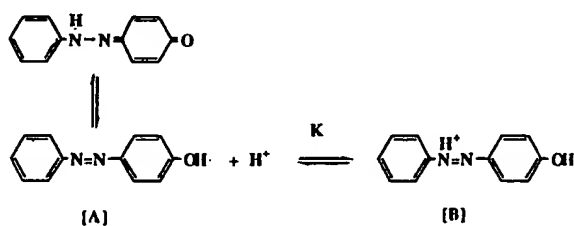
Numbers in the figure mean the ratio of C8 to (C8+TMOS) in mol%

3 結果および考察

スペクトル測定用セル中の溶液は 12 時間以内に全体がゲル化し、さらにゲル中の溶媒がテフロンシールテープを透過して蒸発するため、ゲルの上方から徐々に収縮が起こった。収縮は不均一に進行したので、定量的評価はあえて行わなかった。

ゲル形成時の外観はかすかに黄色を呈していたが、体積収縮が起こった部分から濃い黄色へと変化した。吸収スペクトルを測定すると 460 nm 付近に新しい吸収が現われ、ゲルの収縮にともないそのスペクトル強度が大きくなることがわかった。約 5 日間経過するとゲル全体が均一に収縮した。そのときのスペクトルを図 1 に示す。図から明かなように、C8 の割合が大きくなるにつれて 460 nm 付近のピークが小さくなった。

酸の存在下で HAB は次のような平衡にある^{6)~7)}。



この反応の平衡定数 K は水溶液中で 0.12 と報告されている⁵⁾。[A] と [B] の吸収スペクトルが異なるので、0.1~2.0 モル濃度の塩酸水溶液中の HAB の吸収スペクトル測定からそれぞれの化学種の吸光係数を計算できる⁶⁾。計算結果を図 2 に示す。図か

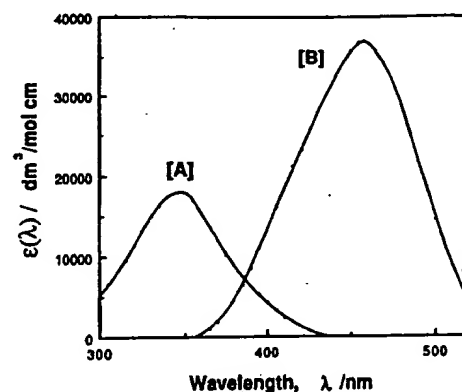


Fig. 2 The respective spectra of the chemical species [A] and [B] obtained from the absorption spectra of HAB in the various pH aqueous solutions

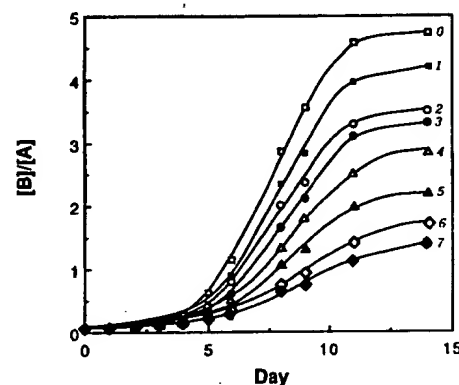


Fig. 3 Plots of [B]/[A] vs. day for various C8-containing silica gels

Numbers in the figure mean the ratio of C8 to (C8+TMOS) in mol%

ら明かなように、[A] の λ_{max} は 346 nm, [B] の λ_{max} は 460 nm となることから、図 1 の結果は C8 の割合の増加にしたがい、[A] の割合が大きくなることを示している。

[A] と [B] の割合の経時変化を図 3 に示す。測定を開始してから 6~7 日後に [B] の割合が急激に増加した。時間の経過は溶媒の蒸発とそれに付随するゲルの収縮を引き起こし、溶媒の蒸発にともない平衡反応が [B] の方へずれると考えられる。図 1 および図 3 は C8 の割合が大きいきとき [A] の方へ平衡が偏ることを示しているが、この理由として次の二つの場合が考えられる。その一つはゲル中に残存する塩化水素の量が少なくなる場合である。すなわち、オクチル基 (疎水性) の割合が大きくなるとゲルは疎水的になるため、ゲル中に残存する塩化水素が少なくなり、[A] の割合が大きくなる場合である。もう一つは、オクチル基の存在により HAB と水素イオンとの反応が妨害される場合である。水溶液中で長鎖の炭化水素鎖をもつ界面活性剤がミセルを形成することはよく知られているが⁹⁾、ゲル中でも疎水性のオク

- 5) I. M. Klotz, H. A. Fiess, J. Y. Chen Ho, M. Mellody *J. Am. Chem. Soc.*, **76**, 5136(1954).
- 6) E. Sawicki, *J. Org. Chem.*, **22**, 365(1957).
- 7) J. C. Merlin, J. L. Lorriaux, E. W. Thomas, A. Papaix, *J. Raman Spectrosc.*, **11**, 209(1981).
- 8) J. H. Collins, H. H. Jaffe, *J. Am. Chem. Soc.*, **84**, 4708(1962).

- 9) J. H. Fendler, E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems", Academic Press, New York(1975).

チル基がミセル状集合体を形成すると考えられ、その集合体中に HAB が溶け込むため水素イオンから隔離されて [A] の割合が大きくなる場合である。

二つの考え方のいずれが妥当であるかを検討するために、水溶液中におけるミセル形成の場合と比較した。阿部らはアゾ色素を SDS (sodium dodecyl sulfate) ミセルまたは非イオン界面活性剤 SDS 混合ミセルに溶解し、その吸収スペクトル測定から色素がミセル中心部に取り込まれることを報告している^{10)~13)}。さらにミセル内では色素が酸化されて退色することを報告している¹⁴⁾¹⁵⁾。シリカゲル中でも、C8 の割合が 7 mol% まで増加するとゲルの色が薄くなり、さらに吸収スペクトル測定でも吸収強度が小さくなることが観察され (図 1), HAB の退色が起こることが示唆された。これはシリカゲル中のミセル状集合体に溶け込んだ HAB のヒドラゾ体が酸化されるために起こるものと考えられている¹⁶⁾。

さらにミセル状集合体の形成について検討を加えた。水溶液中におけるミセル形成の大きな特徴は、臨界ミセル濃度 (cmc) の存在であり、その濃度を越えるとミセルが形成される。また、色素を被可溶化物質として用いると、その溶液の吸収スペクトルは cmc を境に大きく変化する。そこでゲル中の cmc を調べるために、C8 の割合を変化させて吸収スペクトルを測定した (図 4)。なお、横軸の C8 の濃度は TMOS と C8 の全モル数に対する C8 のモル数の百分率で表わした。また、測定データはゲルの体積が安定した 15 日目の吸収スペクトルから求めた。水溶液中におけるミセル形成の場合と同様な急激な吸収スペクトルの変化が確認され、シリカゲル中でオクチル基がミセル状集合体を形成し

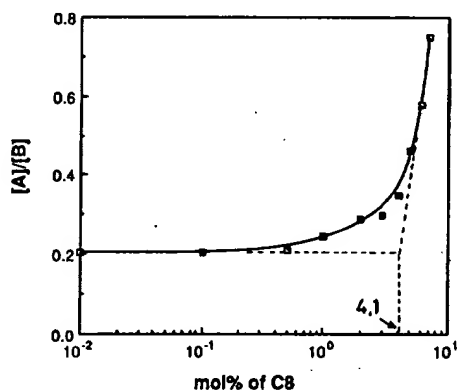


Fig. 4 Plots of [A]/[B] vs. the content of C8 in silica gel after days aging

A steep change appears at 4.1 mol% C8 content

- 10) M. Abe, M. Ohsato, K. Ogino, *Colloid Polym. Sci.*, 262, 657(1984).
- 11) M. Abe, M. Ohsato, N. Suzuki, K. Ogino, *Bull. Chem. Soc. Jpn.*, 57, 831(1984).
- 12) M. Abe, T. Kasuya, K. Ogino, *Colloid Polym. Sci.*, 266, 156(1988).
- 13) K. Ogino, T. Kasuya, M. Abe, *ibid.*, 266, 539(1988).
- 14) K. Ogino, H. Uchiyama, M. Abe, *ibid.*, 265, 52(1987).
- 15) H. Uchiyama, M. Abe, K. Ogino, *ibid.*, 265, 838(1987).
- 16) J. Griffiths, C. Hawkins, *J. Chem. Soc., Perkin II*, 1977, 747.

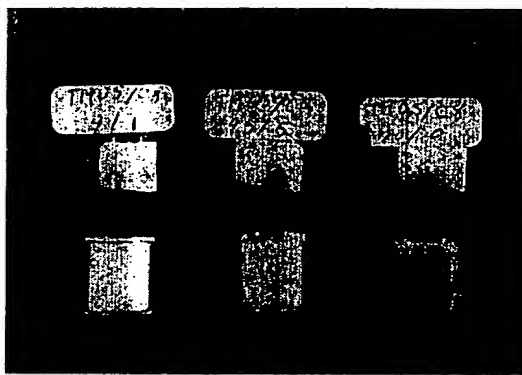


Photo 1 Photos of MBBA-silica composite gels

The silica gel without C8 showed a little shrinkage and MBBA did not exchange completely with the solvent in the gel

ていることがわかった。

ミセル状集合体は、ゲル化の初期においてすでに形成されていると考えることができる。ゲル化反応の初期段階でエステルの加水分解が起こり、オクチルトリヒドロキシシランとテトラヒドロキシシランのエタノール水溶液となる。オクチルトリヒドロキシシランは両親媒性化合物であり、ミセル形成が可能である。ミセルが形成された状態で縮重合が起こり、ゲル化したと考えられるからである。それゆえ、この系の cmc はゾル溶液調製時の濃度で示すのが妥当である。図 4 における [A]/[B] が急激に大きくなる C8 濃度 4.1 mol% からゾル溶液調製時の cmc を求めると 0.13 mol/dm³ となり、オクチル基をもつ界面活性剤の水溶液中におけるミセル形成と同程度の cmc となる¹⁷⁾。

ミセル状集合体の形成は、アルキル基が長くなるほど有利と考えられるので、アルキル基をオクチル基より長くしてみたが、ゲルは白濁してスペクトル測定が不可能であった。そこで本研究ではオクチル基についてのみの検討した。水溶液中におけるミセルは界面活性剤分子が絶えず集合・離散をしているが、シリカゲル中の集合体はオクチル基末端が固定されている。このように固定されたオクチル基は、温度が低下すると分子運動の凍結が起こると考えられるが、-100~100℃ の温度範囲の DSC 測定からは、分子運動の凍結を示唆する現象を検出できなかった。おそらくミセル状集合体を取り囲むシリカの熱伝導が悪いため検出が困難なのであろう。

本研究で作製したシリカゲルは、オクチル基が集合した領域、すなわち疎水性の領域をもち、親油性の有機化合物に対する親和性がよいと考えられる。この特性を応用し、さらにゲルの収縮を抑えることを目的として、ゲル中の溶媒を高沸点の液晶で置換した複合材の作製を試みた。この実験では、液晶分子が分解することを避けるためにゲル合成の触媒である塩酸を加えなかった。触媒無添加の場合、2~3 日でゲル化した。ゲル中の溶媒の蒸発によりゲルの収縮が起こるので、ゲル中の溶媒を不揮発性の液晶と置換すればゲルの収縮は起こらないはずである。ゲル中の空隙を計算し、同体積の MBBA で溶媒の置換を行うことにより、淡黄色の不透明な固体をひび割れが生じることなく得ることができた。これらのゲルの空隙率はほぼ 92% であった。

同様な操作を行うことにより、オクチル基を含まないゲルの場

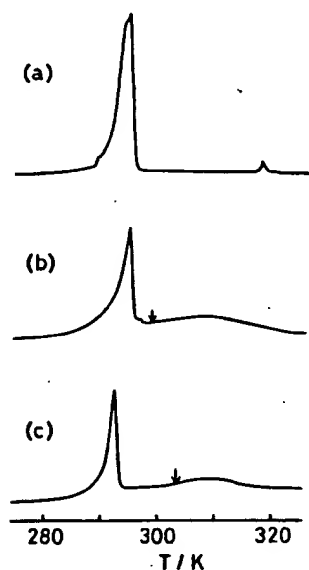


Fig. 5 DSC curves of (a) MBBA, (b) silica gel+MBBA, (c) 5mol% C8-containing silica gel+MBBA

Arrows in the figure show the transition points from a translucent to a transparent state observed on a photomicroscope with an attachment of a hot plate

合でも MBBA を溶かし込むことが可能である。写真 1 にオクチル基の割合を変えて合成したゲルへの MBBA の溶け込む様子を示す。オクチル基を含むゲルの場合では不透明な状態となったが、オクチル基を含まないゲルでは体積が 10~20% 収縮し、添加された MBBA は完全にはゲル中に溶け込まずに残存し、ゲルは完全な不透明とはならなかった。オクチル基を含むゲルの静置安定性はよく、数か月外気にさらしてもほとんど体積変化がなかった。オクチル基を含まないゲルの場合でも MBBA は部分的に溶け込むが、2~3 週間で赤く変色した。これは MBBA とシリカとが直接接合するため、シッフ塩基部分の加水分解が起こり MBBA が変質したものと考えられる。したがって、ゲル中に導入されたアルキル基は液晶を構成している分子をとり囲み、シリカと直接の接触を妨げることにより、液晶を安定に保持されるようにする働きがあるものと思われる。なお、C8 量が 5 mol% 以上のゲルでは一か月経っても変化は認められなかった。

作製した MBBA とシリカゲルとの複合材の場合、その体積の 90% 以上を MBBA が占めているので、MBBA の性質が複合材の性質を決めると考えられる。これら試料の DSC 測定結果を図 5 に示す。なお、測定はあらかじめ試料を 253 K まで急冷し、30 分その温度に保持した後昇温しながら行った。MBBA 単独の場合 (a)、結晶から液晶への転移過程で二つのピーク (吸熱) が重なっていることが認められるが、これは急冷により準安定および安定な固体状態が形成されている¹⁷⁾ためと思われる。いずれの試料でも結晶から液晶への相転移ピークが明瞭に現われたが、その転移温度は C8 量に依存した。

Table 2 Phase transition temperatures of MBBA and its composite gels

Amount of C8 (mol%)	T (K)	
	C→N	N→I
0	295 ^{a)}	299 ^{b)}
2	295 ^{a)}	301 ^{b)}
5	292 ^{a)}	303 ^{b)}
10	292 ^{a)}	301 ^{b)}
MBBA	295 ^{a)}	319 ^{a)}

a) From DSC measurements.

b) From microscopic measurements.

一方、MBBA の液晶から等方性液体への相転移のピーク (319 K) がシリカゲル中で消失し、約 10°C 低いところにブロードなピークが現われた。そこでホットプレート付き顕微鏡で観察したところ白濁状態から透明状態へ 1°C 以内の狭い温度範囲で変化することがわかった。表 2 に測定結果をまとめ、また、図 4 にも顕微鏡観察で得られた温度を矢印で示す。C8 量が 0, 2, 5, 10 mol% のゲルについて比較すると、5 mol% のゲルにおいて白濁状態から透明状態へなる温度が最も高くなった。

これらの現象を考察するために、ゲル中のオクチル基およびシリカが占める体積を計算した。シリカの比重を 2.20、オクチル基の集合部分についてパラフィンの比重 0.90 を採用して計算すると、C8 が 5 mol% のゲルでは体積のほぼ 8% をシリカ相が占め、そのシリカ相の約 25% をオクチル基が占めていることになる。ゲルに溶け込んだ液晶を構成している分子は空隙を満たしているはずである。この空隙は溶媒である水とアルコールが占めていた空間であり、疎水性のオクチル基はこれら溶媒分子に接触しないようになるためミセル状集合体が形成されたはずである。するとゲル中の空隙の方向へオクチル基が向かないこととなり、オクチル基は液晶分子の溶け込みに影響しないこととなる。しかしながら液晶を構成している分子を溶かし込んだ結果からは、オクチル基により液晶を構成している分子が安定に取り込まれることを示している。これらの結果はアルキル基の炭素数が 8 と小さく cmc が 0.13 mol/dm³ と大きいことから説明できよう。すなわちシリカ相中に単分散しているオクチル基の濃度が高く、これらの一部がシリカ相の表面にも存在し、液晶を構成している分子との直接の接触を妨げる働きをしていると考えられる。C8 の割合がさらに高くなると、ミセル状集合体のみならずシリカ表面に多くのオクチル基が分布し、液晶を構成している分子はオクチル基と混合し、凝固点降下と同様な効果により相転移の温度が下がったものと思われる。一方、C8 が 0 mol% の場合では、MBBA 分子とシリカとの直接接触するようになり、液晶形成が困難になると考えられる。

4 結 論

オクチル基を含むシリカゲルの合成を行い、オクチル基がミセル状集合体を形成することを明らかにし、このようなゲル中に疎水性かつ高沸点の液晶物質が安定に取り込まれることを見いだした。このようにして作製された無機-有機複合ゲルは、温度上昇による白濁状態から透明状態への転移が観測され、ゲル中に溶かし込まれた液晶の性質が保持されていることになる。とくに疎水性の炭化水素鎖を導入することにより、取り込まれた分子の安

17) J. Mayer, T. Aluga, J. A. Janik, *Phys. Lett.*, 41 A, 102 (1972).

定性を高めることができることがわかった。さらに高沸点の化合物を溶かし込むことによりゲルの収縮を抑制することが可能となり、種々の機能をもつ有機-無機複合材料が作製できることが示

唆された。

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**Special Articles on
Synthesis and Supramolecular Structure
of Functionality Amphiphiles**

**Preparation of Silica Gels Containing Hydrophobic Hydrocarbon
Chains and Their Structures**

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Silica gels containing hydrophobic hydrocarbon chains were prepared from tetramethoxysilane (TMOS) and octyltrimethoxysilane (C8) by means of sol-gel process. As the hydrophobic hydrocarbon chains were expected to form micelle-like aggregates in the inorganic silica matrix, similar to the ordinal micelles in an aqueous surfactants solution, a dye (4-hydroxyazobenzene; HAB) was used to monitor the structure change in the silica gel by an addition of hydrophobic octyl groups. As a result formation of micelle-like aggregates was strongly suggested. Moreover, solubilization of organic compound into the C8-containing silica gel was carried out to make new organic-inorganic composite material. A liquid crystal (*N*-(4-methoxybenzylidene)-4-butylaniline; MBBA) was used for this purpose and the thermal properties of the composite materials were studied.

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PREPARATION OF SILICA GELS CONTAINING HYDROPHOBIC
HYDROCARBON CHAINS AND THEIR STRUCTURES

Shigetoshi Nakamura et al.

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1. Introduction

In recent years, many research reports on the synthesis of inorganic materials using the sol-gel method have been published ¹⁾. In many of these, a gel of a desired composition is prepared by the sol-gel method. Afterwards, by high-temperature

heat treatment of the gel, an inorganic material having the desired composition is synthesized. The gel prepared by the sol-gel method is porous. As such, the mechanical strength is low. Furthermore, with the evaporation of the solvent from the gel, the volume shrinks. By the high-temperature heat treatment, a dense, strong material is obtained.

The sol-gel method has a major characteristic in that an inorganic material can be synthesized at a relatively low temperature such as room temperature. As one direction to revive this characteristics ¹ the synthesis of an organic-inorganic composite material has been considered²⁾⁻⁴⁾. Unless the high-temperature heat treatment operation is carried out, the synthesis of a new composite material containing an organic compound in an inorganic material is possible. In the present research, the synthesis of silica gel containing a C₈ octyl group as a long hydrocarbon chain was carried out. The aggregate state of formation of a hydrocarbon chain in silica gel was investigated. Furthermore, by the solubilization of liquid crystals in the synthesized silica gel, the preparation of a material with temperature response characteristics and gel shrinkage inhibition were investigated.

2. Experimental

2.1 Synthesis of silica gel containing an octyl group and its structural analysis ¹

Tetramethoxysilane (TMOS: Petrarch Systems), octyltrimethoxysilane (C8: Petrarch Systems), and 4-hydroxyazobenzene (HAB: Tokyo Kasei, special grade) were

purchased and used as such. HAB was dissolved in dried ethanol to make Solution A of 0.05 mmol/dm^3 . TMOS 2.44-2.60 g and C8 0-0.4 g were accurately weighed and mixed well in 10-mL sample bottles. The ratios of TMOS and C8 are shown in Table 1. Furthermore, 1.6 mL of Solution A and 1.43 mL of 13 wt% hydrochloric acid were added. Mixing was carried out with a vibrator. Heat evolved at this time. After standing a few minutes, the temperature decreased to room temperature or so. Solutions were placed in a 10 mm x 10 mm square polymethacrylate UV cell (Hellma) and sealed with Teflon seal tape (Nichias, thickness 0.1 mm). Pure water was used as a reference. Spectra were measured with a Hitachi 340 ultraviolet visible spectrometer at 300-600 nm.

2.2. Preparation of silica gel containing liquid crystals

In 10-mL sample bottles, 2.44-2.60 g of TMOS, 0-0.4 g of C8, 1.6 mL of ethanol, and 1.2 mL of pure water were mixed, enclosed and allowed to stand at room temperature. Without the addition of the catalyst (hydrochloric acid), it took 2-3 days for gelatin [formation]. An appropriate amount of anhydrous ethanol was added dropwise from above the gel. On the following day, this ethanol was discarded and replaced with new ethanol. This operation was repeated more than 5 times so that the solvent in the gel was replaced with ethanol. In this process, no volumetric change of the gel was observed.

Next, ethanol in the gel mentioned previously was replaced by liquid crystals. For the amount of liquid crystals required for replacement, the volume of SiO_2 (specific gravity 2.20) formed from TMOS during the reaction solution preparation was calculated beforehand. This volume was subtracted from the volume

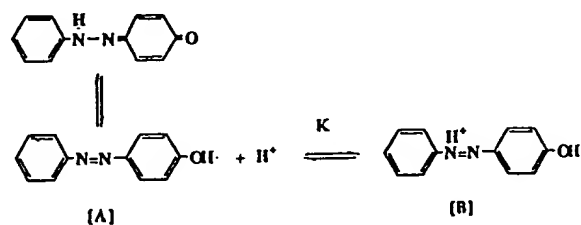
of the entire gel to determine the porosity. As the liquid crystals, N-(4-methoxybenzylidene)-4-butyraniline (MBBA; Aldrich Chem., specific gravity 1.027) was used. If the stopper is placed loosely [on the bottle], MBBA will penetrate into the gel with the evaporation of ethanol. After 2-3 days pass, a light yellow solid will be obtained. In the DSC measurements, a Perkin Elmer DSC-II was used. Measurements were made under a nitrogen atmosphere at a heating rate of 5 C/min.

3. Results and observations

The solution in the spectrum measuring cell completely gelled within 12 h. Furthermore, since the solvent in the gel evaporated through the Teflon seal tape, shrinkage occurred slowly from the top of the gel. Since the shrinkage proceeded nonuniformly, quantitative evaluation was not carried out.

The color during gel formation was faintly yellow. The portion with the volumetric shrinkage changed to a dark yellow color. With the determination of the absorption spectrum, a new absorption appeared near 460 nm. It was found that, with the shrinkage of the gel, this spectral intensity increased. After about 5 days had elapsed, the entire gel had a uniform shrinkage. The spectra at that time are shown in Figure 1. As shown by the figure, with an increase in the level of C8, the peak near 460 nm became smaller.

In the presence of an acid, HAB has the following equilibria ⁵⁾⁻⁷⁾.



The equilibrium constant K of this reaction was reported to be 0.12 in an aqueous solution ⁵⁾. Since the absorption spectra of [A] and [B] are different, the absorption coefficients of each chemical species can be calculated from the absorption spectral measurements of HAB in a hydrochloric acid aqueous solution at 0.1-2.0 molar concentration⁸⁾. The calculated results are shown in Figure 2. As shown in the figure, λ_{max} of [A] was 346 nm, and λ_{max} of [B] was 460 nm. The results of Figure 1 show that the level of [A] increases with an increase in the level of C8.

The temporal change of the ratio of [A] and [B] is shown in Figure 3. After 6-7 days following the initiation of the measurements, the ratio of [B] increases drastically. With the elapse of time, evaporation of the solvent and shrinkage of the gel accompanying evaporation occurred. With the evaporation of the solvent, it is believed that the equilibrium reaction shifts to [B]. Figure 1 and Figure 3 show that the equilibrium shifts to [A] when the level of C8 is increased. As for reasons, the following two cases can be considered. One of them is the case in which the amount of hydrogen chloride remaining in the gel is decreased. In other words, if the level of the octyl group

(hydrophobic) is increased, since the gel is hydrophollic the hydrogen chloride remaining in the gel is decreased and the level of [A] is increased. The other is a case in which the reaction between HAB and hydrogen ions is hindered by the presence of the octyl group. The formation of micelles by a surfactant having a long hydrocarbon chain in an aqueous solution is well known ⁹⁾. However, it is believed that, even in the gel, the hydrophobic octyl groups form a micelle-type aggregate. Since HAB is solubilized in the aggregate, it is isolated from hydrogen ions and the ratio of [A] is increased.

In order to investigate which one of the two concepts was appropriate, a comparison was made with the case of micelle formation in aqueous solution. Abe et al. dissolved an azo coloring matter in SDS (sodium dodecyl sulfate) micelle or a nonionic surfactant SDS mixed micelle, and reported ¹⁰⁾⁻¹³⁾ that the coloring matter was absorbed in the central portion of the micelle based on its absorption spectrum measurement. It was further reported ¹⁴⁾⁻¹⁵⁾ that the coloring matter was oxidized inside the micelle so that fading occurred. Even in silica gel, if the content of C8 was increased to 7 mol %, the color of the gel was light. Furthermore, it was observed that the absorption intensity decreases even in the absorption spectrum measurement (Figure 1). This suggested that fading of HAB occurred. This is believed to occur¹⁶⁾ owing to the oxidation of the hydrazo body of the HAB solubilized in the micelle aggregate in the silica gel.

Furthermore, the investigation on the formation of the micelle aggregate was conducted. The major characteristic of micelle formation in an aqueous solution is the presence of the critical micelle concentration (cmc). If such a concentration is exceeded, micelle will be formed. Furthermore, if a coloring

matter is used as a solubilized substance, the absorption spectrum of its solution will change to a large extent in the vicinity of cmc. In order to investigate cmc in the gel, the content of C8 was varied and the absorption spectrum was measured (Figure 4). The concentration of C8 on the abscissa was expressed as the percentage of the number of moles of C8 with respect to the total number of moles of TMOS and C8. Furthermore, the measured data were determined from the absorption spectra on the 15th day when the volume of the gel had stabilized. A drastic change in the absorption spectrum was observed in the same manner as in the case of micelle formation in the aqueous solution. It was found that the octyl group formed a micelle aggregate in silica gel.

It can be postulated that the micelle-type aggregate has already been formed in the initial period of gelation. In the initial stage of the gelation reaction, the hydrolysis of the ester occurs to form an ethanol aqueous solution of octyltrihydroxysilane and tetrahydroxysilane. The octyltrihydroxy-silane is an amphiphilic compound, capable of micelle formation. Polycondensation occurs in the state of micelle formation presumably due to gelation. Therefore, it is appropriate that the cmc of this system is represented by the sol concentration during the sol solution preparation. The cmc during the solution preparation from a C8 concentration of 4.1 mol% when $[A]/[B]$ increased abruptly in Figure 4 was determined to be 0.13 mol/dm^3 . It was about the same cmc for micelle formation in the aqueous solution of the surfactant having the octyl group⁹⁾.

It was postulated that the formation of the micelle aggregate would be more advantageous if the alkyl group was longer. An alkyl group longer than the octyl group was tried.

However, the gel was white and turbid and spectral measurement was impossible. Therefore, in the present research, only the octyl group was investigated. For the micelle in the aqueous solution, the surfactant molecules were continuously aggregated and dispersed. However, for the aggregate in silica gel, the octyl group terminal was fixed. It was believed that, for the octyl group fixed in this manner, freezing of the molecular movement would occur when the temperature was decreased. However, from DSC measurements in a temperature range of -100 to 100 C, a phenomenon suggesting freezing of the molecular movement could not be detected. Possibly, the detection was difficult because the thermal conduction of silica surrounding the micelle aggregate was poor.

The silica gel prepared in the present research has a region of aggregation of octyl groups, that is, a hydrophobic region. The affinity with respect to oleophilic organic compounds is considered to be good. By the application of this characteristic and with an objective to inhibit shrinkage of the gel, an attempt was made to prepare a composite material obtained by the substitution of the solvent in the gel by liquid crystals with a high boiling point. In this experiment, in order to avoid the decomposition of liquid crystal molecules, hydrochloric acid as a catalyst for gel synthesis was not added. In the case without the catalyst addition, gelation occurred in 2-3 days. Since shrinkage of gel occurs owing to the evaporation of the solvent in the gel, it was expected that shrinkage of the gel would not occur if the solvent in the gel was replaced by involatile liquid crystals. Porosity in the gel was calculated. By carrying out the substitution of the solvent with the same volume of MBBA, it was

possible to obtain a light yellow opaque solid without the formation of cracks. The porosity of this gel was about 92%.

By carrying out the same operation, the solubilization of MBBA was possible even in the case without octyl groups. Photo 1 shows the manner of solubilization of MBBA into gels synthesized by changing the content of the octyl groups. In the case of the gel containing octyl groups, the volume shrank by 10-20 %. The added MBBA remained without solubilization in the gel at all, and the gel was not completely opaque. The static stability of the gel containing octyl groups was good. Even if it was exposed to the atmosphere for several months, there was essentially no volumetric change. Even in the case of the gel containing no octyl groups, MBBA was partly solubilized and it became red in 2-3 weeks. This was believed to be due to the fact that the hydrolysis of the Schiff base portion occurred and MBBA changed its properties because of direct contact between MBBA and silica. Therefore, the alkyl groups introduced into the gel surround the molecules constituting the liquid crystals. Hindrance of direct contact with silica is believed to play a role in maintaining the liquid crystals in a stable manner. For the gel with a C8 content of more than 5 mol%, no change was observed even after one month.

In the case of a prepared composite material of MBBA and silica gel, since more than 90% of its volume was occupied by MBBA it is believed that the properties of MBBA decide the properties of the composite material. The DSC measured results of samples are shown in Figure 5. The measurements were carried out during heating after quenching of the sample to 253 K beforehand and maintaining it at this temperature for 30 min. In the case of MBBA alone (a), it was found that two peaks (endothermis) overlapped in the transition from crystals to liquid crystals.

This is believed to be due to the fact that pseudo stable and stable solid states are formed by quenching¹⁷⁾. For any of the samples, the phase transition peak from crystals to liquid crystals appeared clearly. However, its transition temperature depended on the C8 content.

On the other hand, the peak (319 K) for the phase transition from the liquid crystals of MBBA to the isotropic liquid vanished in the silica gel. At a location about 10 C lower, a broad peak appeared. By observations with a microscope equipped with a hot plate, a change was found from a white turbid state to a transparent state in a narrow temperature range less than 1 C. The measured results are summarized in Table 2. The temperatures obtained in the microscopic observations are shown by arrows in Figure 4. A comparison was made for the gels with C8 contents of 0, 2, 5 and 10 mol%. The temperature of change from the white turbid state to the transparent state for the gel with 5 mol% was the highest.

In order to investigate these phenomena, the volumes occupied by octyl groups and silica in the gel were calculated. Calculations were made by the adoption of 2.20 for the specific gravity of silica and 0.90 as the specific gravity of paraffin in the aggregate portion of the octyl groups. For the gel with 5 mol% C8, about 8% of the volume was occupied by the silica phase. About 25% of the silica phase was occupied by the octyl groups. It is believed that the molecules constituting the liquid crystals solubilized in the gel fill the pores. These pores are the spaces occupied by water and alcohol as the solvents. It is believed that a micelle aggregate has been formed since the hydrophobic octyl groups are not in contact with these solvent molecules. In doing this, the octyl groups do not face in the

direction of the pores in the gel, and the octyl groups do not affect the solubilization of liquid crystal molecules. However, the results of the solubilization of molecules constituting the liquid crystals show that the molecules constituting the liquid crystals of the octyl groups are taken in stably. These results can be explained by the fact that the number of carbon atoms of the alkyl group is less than 8 and cmc is larger than 0.13 mol/dm^3 . In other words, it can be postulated that the concentration of the octyl groups monodispersed in the silica phase is high and that part of these also exist on the surface of the silica phase. They play a role in inhibiting direct contact of the silica with the molecules constituting the liquid crystals. If the content of C8 is further increased, many octyl groups will distribute not only on the micelle aggregate but also the silica surface. It is believed that the molecules constituting the liquid crystals mix with the octyl groups, and the temperature of the phase transition is decreased by the same effect as freezing point depression. On the other hand, in the case of C8 at 0 mol%, MBBA molecules and silica are in direct contact and liquid crystal formation is presumably difficult.

4. Conclusions

The synthesis of silica gel containing octyl groups was carried out. The formation of a micelle aggregate by the octyl groups was clarified. It was found that a hydrophobic liquid crystal substance with a high boiling point was taken in stably in such a gel. For the inorganic-organic composite gel prepared in this manner, a transition from the white turbid state to the transparent state due to a temperature rise was observed. The

properties of the liquid crystals insolubilized in the gel were maintained. In particular, by the introduction of hydrophobic hydrocarbon chains, it was found that the stability of the molecules taken in was increased. Furthermore, by the solubilization of a high boiling point compound, it was possible to inhibit the shrinkage of the gel. This suggests that an organic-inorganic composite material having a variety of functions can be prepared.

1) Masuo Sakuhana, "Science of the sol-gel process", Magne Jofu Sha (1988)

4) Toshiro Tani, Ceramics 21, 111 (1989)

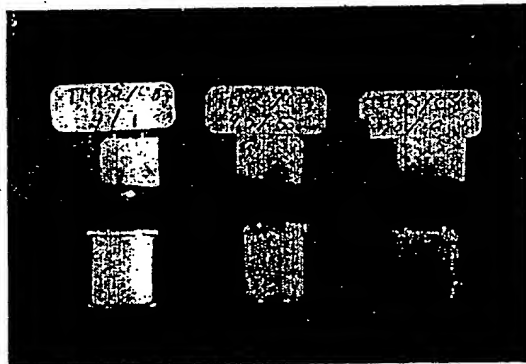


Photo 1 Photos of MBBA-silica composite gels

The silica gel without C8 showed a little shrinkage and MBBA did not exchange completely with the solvent in the gel

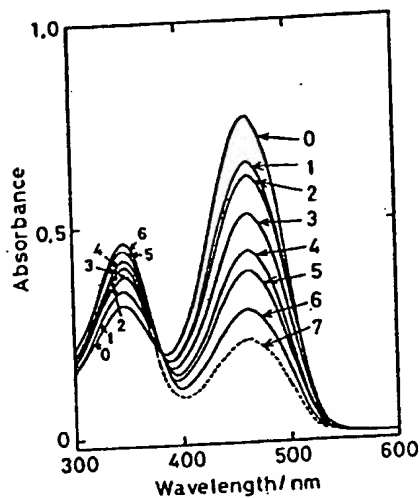


Fig. 1 Absorption spectra of HAB solubilized in C8-containing silica gels

Numbers in the figure mean the ratio of C8 to (C8+TMOS) in mol%

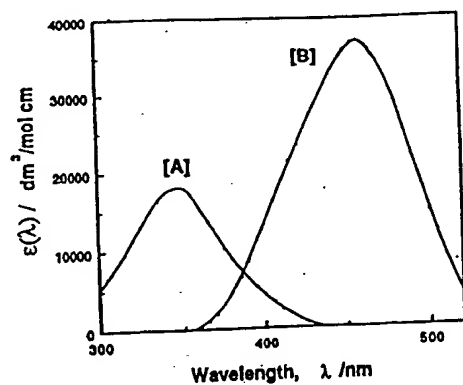


Fig. 2 The respective spectra of the chemical species [A] and [B] obtained from the absorption spectra of HAB in the various pH aqueous solutions

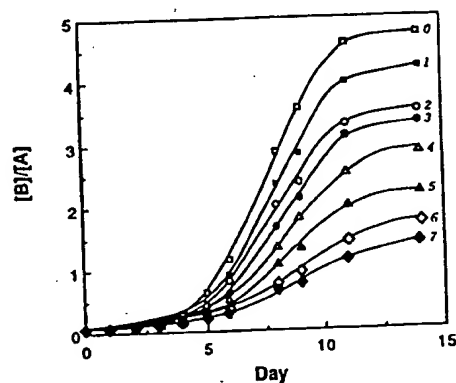


Fig. 3 Plots of $[B]/[A]$ vs. day for various C8-containing silica gels

Numbers in the figure mean the ratio of C8 to (C8+TMOS) in mol%

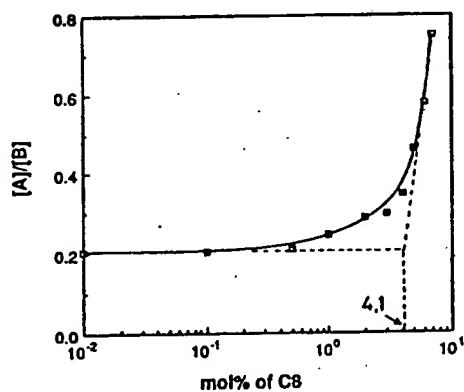


Fig. 4 Plots of $[A]/[B]$ vs. the content of C8 in silica gel after days aging

A steep change appears at 4.1 mol% C8 content

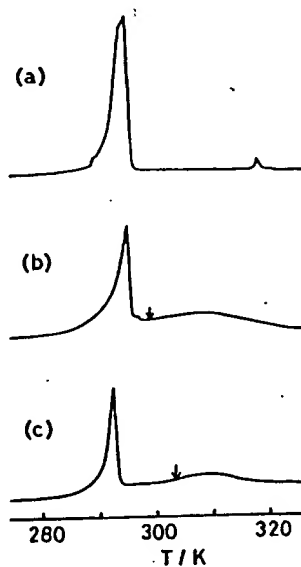


Fig. 5 DSC curves of (a) MBBA, (b) silica gel+MBBA, (c) 5mol% C8-containing silica gel+MBBA

Arrows in the figure show the transition points from a translucent to a transparent state observed on a photomicroscope with an attachment of a hot plate

Table 1 Preparation conditions of samples

Amount of C 8(mol%)	TMOS (g)	C 8 (g)	Ethanol (ml)	HCl ^{a)} (ml)
0	2.60	0	1.6	1.4
1	2.57	0.042	1.6	1.4
2	2.55	0.094	1.6	1.4
3	2.52	0.141	1.6	1.4
4	2.50	0.188	1.6	1.4
5	2.47	0.235	1.6	1.4
6	2.44	0.282	1.6	1.4
7	2.42	0.329	1.6	1.4

a) 13.2 wt% HCl solution.

Table 2 Phase transition temperatures of MBBA and its composite gels

Amount of C 8(mol%)	T(K)	
	C→N	N→I
0	295 ^{a)}	299 ^{b)}
2	295 ^{a)}	301 ^{b)}
5	292 ^{a)}	303 ^{b)}
10	292 ^{a)}	301 ^{b)}
MBBA	295 ^{a)}	319 ^{a)}

a) From DSC measurements.

b) From microscopic measurements.

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